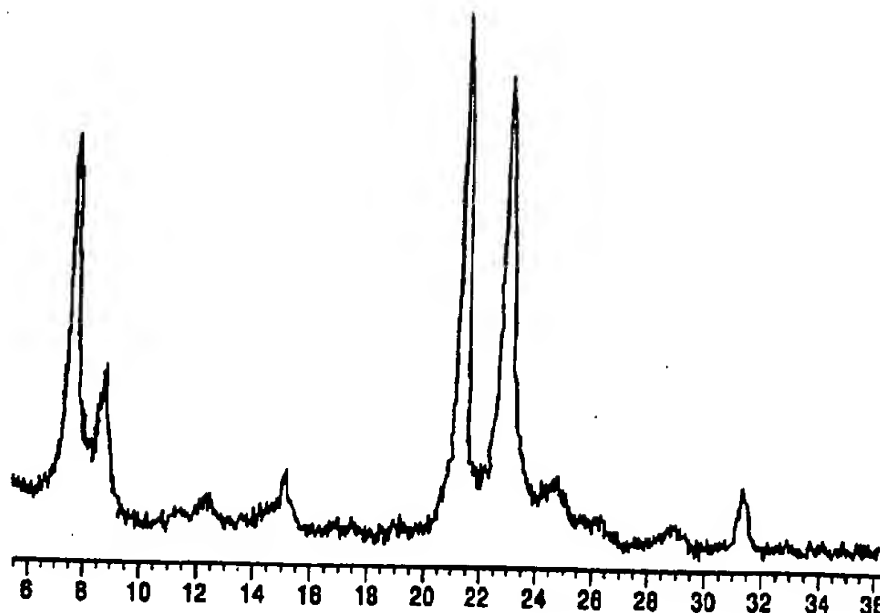


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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01B 39/48	A1	(11) International Publication Number: WO 99/35087 (43) International Publication Date: 15 July 1999 (15.07.99)
(21) International Application Number: PCT/US99/00236 (22) International Filing Date: 7 January 1999 (07.01.99) (30) Priority Data: 09/005,969 12 January 1998 (12.01.98) US (71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US). (72) Inventors: KENNEDY, Carrie, Lynn; 1773 Harrison Court, Turnersville, NJ 08012 (US). ROLLMANN, Louis, Deane; 211 S. Washington Avenue, Moorestown, NJ 08057 (US). SCHLENKER, John, Lee; 7 Hillside Road, Thorofare, NJ 08086 (US). (74) Agents: ROBERTS, Peter, W. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).	(81) Designated States: IN, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	

(54) Title: SYNTHESIS OF ZSM-48



(57) Abstract

A method for preparing ZSM-48 comprises: a) preparing a reaction mixture comprising a source of silica, a source of trivalent metal oxide, an alkali metal oxide and a directing agent of ethylenediamine in a solvent phase comprising water, wherein the mixture, in terms of mole ratios of oxides, has the following composition ranges: $\text{SiO}_2/\text{Me}_2\text{O}_3$: 100 to 1500, M/SiO_2 : 0 to 0.4, RN/SiO_2 : 1.0 to 5.0, OH^-/SiO_2 : 0 to 0.3, and $\text{H}_2\text{O}/\text{SiO}_2$: 10 to 100, wherein Me is trivalent metal, M is alkali metal and RN is ethylenediamine; and b) maintaining the mixture under crystallization conditions until crystals of ZSM-48 are formed.

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SYNTHESIS OF ZSM-48

This invention relates to synthesis of ZSM-48 having a new crystal morphology.

U.S. Patent No. 4,423,021 to Rollmann et al. describes a method for synthesizing
5 ZSM-48 using a diamine having four to twelve carbons as the directing agent. The composition is described as a crystalline silicate and it includes very little, if any aluminum.

U.S. Patent Nos. 4,397,827 and 4,448,675 to Chu also describes method for synthesizing ZSM-48 including very little, if any, aluminum. The synthesis utilizes a mixture of an amine having from two to twelve carbons and tetramethylammonium compound as the
10 directing agent.

U.S. Patent No. 5,075,269 to Degnan et al. describes ZSM-48 prepared with an organic linear diquatery ammonium compound as the directing agent. The crystal morphology is illustrated in Figures 3 and 4 of the patent and is described as having platelet-like crystal morphology at high silica/alumina molar ratios and aggregates of small irregularly
15 shaped crystals at silica/alumina molar ratios below 200. In 5,075,269 this is compared with the crystal morphology of Rollmann et al. (U.S. Patent No. 4,423,021) in Figure 1 and Chu (U.S. Patent No 4,397,827) in Figure 2. Figures 1 and 2 show a rod-like or needle-like crystal morphology which is random and dispersed.

ZSM-48 is also described by R. Szostak, Handbook of Molecular Sieves, Van
20 Nostrand Rheinhold, New York 1992, at pp. 551-553. Organic directing agents suitable for the synthesis of ZSM-48 are listed as diquat-6, bis (N-methylpyridyl)ethylinium, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 1, 4, 8, 11-tetra-aza-undecane, 1, 5, 9, 13-tetra-aza-undecane, 1, 5, 8, 12-tetra-aza-undecane, 1, 3-diaminopropane, n-propylamine/TMA⁺, hexane-diamine and triethylamine. There is no
25 suggestion of ethylenediamine. In addition, the crystal habit is described therein as bundles of needles and there is no suggestion of radial morphology.

Accordingly, the prior art utilizes relatively complex and expensive organics. It is an object of the present invention to overcome disadvantages of the prior art using a less expensive and more readily available directing agent to make ZSM-48. This reduces
30 manufacturing costs and provides a superior ZSM-48 product.

The present invention relates to a method for preparing ZSM-48, preferably exhibiting radial aggregate morphology, which comprises:

(a) preparing a reaction mixture comprising a source of silica, a source of trivalent metal oxide, an alkali metal oxide and a directing agent of ethylenediamine in a solvent phase comprising water,

wherein said mixture, in terms of mole ratios of oxides, has the following composition ranges:

$\text{SiO}_2/\text{Me}_2\text{O}_3$: 100 to 1500,

M/SiO_2 : 0 to 0.4,

RN/SiO_2 : 1.0 to 5.0,

OH/SiO_2 : 0 to 0.3, and

$\text{H}_2\text{O}/\text{SiO}_2$: 10 to 100,

wherein Me is trivalent metal, M is alkali metal and RN is ethylenediamine; and

(b) maintaining said mixture under crystallization conditions until crystals of said ZSM-48 are formed.

The zeolite ZSM-48 prepared by the method of the present invention, while exhibiting the same X-ray characteristics of the conventionally prepared ZSM-48, frequently possesses a surprisingly different crystal morphology. The ZSM-48 of the present invention is less fibrous than many conventionally prepared ZSM-48 crystals. By fibrous is meant crystals in the form of individual rods or needles, whose length is at least 5 and often at least 10 times their diameter. A ZSM-48 prepared with ethylenediamine directing agent can possess a radial aggregate morphology. The resulting morphology can be described as sea urchin-like. ZSM-48 crystals prepared by conventional prior art methods possess a dispersed or bundled rod or needle-like morphology or platelet morphology.

The as-synthesized ZSM-48 product is also low in alkali metal ion, and after calcination to remove the organic, advantageously can be used as an acidic catalyst component without ion exchange.

The X-ray diffraction pattern of ZSM-48 has the significant lines shown in Table 1 and is further characterized by the fact that it exhibits only a single line within the range of 11.8 ± 0.2 Angstrom units. The presence of only a single line at the indicated spacing structurally distinguishes the material from closely related material such as ZSM-12 (U.S. Patent No. 3,832,449) which has a doublet (two lines) at 11.8 ± 0.2 Angstrom units, and high silica ZSM-12 (U.S. Patent No. 4,104,294) which also exhibits a doublet at 11.8 ± 0.2 Angstrom units.

TABLE 1	
Characteristic Lines of ZSM-48	
d(A)	Relative Intensity (I/I ₀)
11.8 +/- 0.2	W-VS
10.2 +/- 0.2	W-M
7.2 +/- 0.15	W
4.2 +/- 0.08	VS
3.9 +/- 0.08	VS
3.6 +/- 0.06	W
3.1 +/- 0.05	W
2.85 +/- 0.05	W

These values were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a diffractometer equipped with a scintillation counter with a strip chart pen record was used. The peak heights, intensity (I), and the positions as function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities, 100 I/I₀, where I₀ is the intensity of the strongest line or peak, and d (obs.), the interplanar spacing in A, corresponding to the recorded lines, were calculated. In Table 1 the relative intensities are given in terms of the symbols W for weak, VS for very strong and W-S for weak-to-strong (depending on the cationic form). Ion exchange of the sodium ion with cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variations in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample, as well as if it has been subjected to thermal treatment.

The composition of the as-synthesized ZSM-48 prepared by the method of the present invention can be identified, in terms of moles of anhydrous oxides per 100 moles of silica as follows:

(2 to 10) RN: (0 to 1.0)M₂O: (0.06 to 1)Me₂O₃: (100)SiO₂

wherein RN is an ethylenediamine, M is at least one alkali metal cation, Me₂O is an oxide of a trivalent metal, e.g., aluminum, titanium, iron, chromium, zirconium, vanadium, molybdenum, arsenic, antimony, manganese, gallium, germanium, boron, etc. or combination thereof.

- 5 The ZSM-48 of the present invention can be prepared from a crystallization reaction mixture containing a source of silica, an alkali metal (M) oxide or source thereof such as sodium silicate, alkali salt or alkali hydroxide, an organic directing agent of ethylenediamine RN, optionally a source of metal oxides Me₂O₃ or source thereof such as alumina gel, aluminum sulfate, iron sulfate, zirconyl chloride, gallium oxide, germania, titanyl chloride,
10 boria, vanadia, chromia, molybdena, etc. and a solvent phase which includes water. Suitable alkali metals include, e.g., sodium, lithium, and potassium.

The reaction mixture, in terms of mole ratios of oxides, has the following composition ranges:

REACTANTS	BROAD	PREFERRED
SiO ₂ /Al ₂ O ₃	100 to 1500	150 to 500
M/SiO ₂	0 to 0.4	0.001 to 0.10
RN/SiO ₂	1.0 to 5.0	2.0 to 4.0
OH ⁻ /SiO ₂	0 to 0.3	0.001 to 0.10
H ₂ O/SiO ₂	10 to 100	15 to 40

15

While it is not intended to be bound by theory, it is believed that the organic directing agent should be present in the crystallizing reaction mixture in an amount sufficient to fill the pores of the zeolite as they are being formed.

- Ethylenediamine is generally an alkaline liquid soluble in water and which, besides
20 acting as an organic directing agent in the method of the present invention, can also be considered to form part of the solvent phase for crystallization, along with water. It is recognized that a fraction of the amine functional groups may be protonated.

The amount of ethylenediamine in the solvent phase of the resulting mixture is important in producing a pure ZSM-48 crystal. In general, if the amount of ethylenediamine in the solvent phase is 20 mole percent or above, the resulting crystal will not be a pure ZSM-48 crystal, i.e., the resulting crystal will contain a different crystalline aluminosilicate, such as ZSM-5. Often, if the amount of ethylenediamine in the solvent phase is less than 8 mole %, the resulting crystal will also not be a pure ZSM-48 crystal, i.e., the resulting product is either less than 100% ZSM-48 crystal or simply amorphous.

The optimal amount of RN in the solvent phase is particularly dependent on such parameters as $\text{SiO}_2/\text{Me}_2\text{O}_3$ ratio, the presence of seeds, (usually added at 1-5%, based on silica) and the OH^-/SiO_2 ratio. At very high $\text{SiO}_2/\text{Me}_2\text{O}_3$ ratio, e.g., above 500, less RN is required, and 5 to 10% may be satisfactory. At lower $\text{SiO}_2/\text{Me}_2\text{O}_3$ ratio, more RN is required, e.g., 8 to 15%.

Crystal morphology is also sensitive to variation in these parameters. For example, lower OH^-/SiO_2 ratios, e.g., below 0.05 are particularly preferred in order to obtain the radial aggregate crystal morphology.

The crystallization mixture of the present invention has a pH value preferably from 7 to 14, more preferably from 11 to 13.

The crystallization mixture of the present invention is maintained at a temperature range of 100 to 200°C, preferably from 140 to 170°C, until crystals of the material are formed, typically from 0.5 hour to two weeks. Thereafter, the ZSM-48 crystals are separated from the liquid and recovered.

The resulting ZSM-48 of the present invention has a low alkali metal ion content, typically containing from 0 to 1.0, and more usually from 0.05 to 0.5, sodium ions per unit cell and can be used as an active catalyst without ion exchange.

However, if desired, the original cations can be replaced, at least in part, by calcination and/or ion exchange with other cations according to techniques well known in the art. Thus, the original cations can be exchanged into a hydrogen or hydrogen ion precursor form such as ammonium or a form in which the original cation has been replaced by cations of rare earth metals, manganese, calcium, as well as metals of Groups II through VIII of the Periodic Table. Thus, for example, the original cations can be exchanged with ammonium ions or with hydronium ions. Catalytically active forms of these would include, in particular, hydrogen, rare earth metals, aluminum, metals of Groups II, e.g., zinc, and VIII, e.g., nickel, platinum

and palladium of the Periodic Table and manganese. Typical ion exchange techniques include contacting the zeolite with a salt of the desired replacing cation. Although a variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates.

Representative ion-exchange techniques are disclosed in a wide variety of patents
5 including U.S. Patent Nos. 3,140,249, 3,140,251 and 3,140,253.

The ZSM-48 of the present invention can also be used as a catalyst in intimate combination with an additional hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed.
10 Such component can be exchanged into the composition, impregnated therein or physically intimately admixed therewith. Such component can be impregnated in or onto it such as, for example, by, in the case of platinum, treating with a solution containing platinum metal-containing ions. Thus, suitable platinum compounds include chloroplatinic acid, platinous chloride and various compounds containing the platinum ammine complex.

15 The ZSM-48 when employed either as an adsorbent or as a catalyst in one of the aforementioned processes should be dehydrated, at least partially. This can be done by heating to a temperature in the range of 100 to 600°C in an atmosphere, such as air, nitrogen, etc. and at atmospheric pressure from between about 1 and about 48 hours. Dehydration can also be performed at room temperature merely by placing the ZSM-48 type catalyst in a vacuum, but
20 a longer time is required to obtain a sufficient amount of dehydration.

As is the case with many catalysts, it is desired to incorporate the ZSM-48 with another material resistant to the temperatures and other conditions employed in organic conversion processes. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal
25 oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the composition of the present invention, i.e., combined therewith which is active, tends to improve the conversion and/or selectivity of the catalyst in certain organic conversion processes. Inactive materials suitably serve as diluents to control the amount of conversion in
30 a given process so that products can be obtained economically and without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally-occurring clays, e.g., bentonite and kaolin, to improve the crush strength of the catalyst under

commercial operating conditions. Such material, i.e., clays, oxides, etc., function as binders for the catalyst. It is desirable to provide a catalyst having good crush strength because in a petroleum refinery the catalyst is often subjected to rough handling, which tends to break the catalyst down into powder-like materials, which cause problems in processing. These clay
5 binders have been employed for the purpose of improving the crush strength of the catalyst.

Naturally-occurring clays which can be composited with the ZSM-48 of the present invention include montmorillonite and kaolin families. These families include subbentonites, and kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauzite. Such
10 clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. Binders useful for compositing with the zeolite of the present invention also include inorganic oxides, notably alumina.

In addition to the foregoing materials, the zeolite of the present invention can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-
15 zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The relative proportions of finely divided ZSM-48 and inorganic oxide gel matrix vary widely with the ZSM-48 content ranging from 1 to 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to
20 70 percent by weight of the composite.

Employing a catalytically active form of the composition of this invention which contains a hydrogenation component, reforming stocks can be reformed employing a temperature of 300 to 600°C. The pressure can be from 100 to 1,000 psig (800 to 7000 kPa) but is preferably from 200 to 700 psig (1500 to 4900 kPa). The liquid hourly space velocity is
25 generally from 0.1 to 10, preferably from 0.5 to 4 and the hydrogen to hydrocarbon mole ratio is generally from 1 to 20, preferably from 4 to 12.

The catalyst made with the ZSM-48 can also be used for hydroisomerization of normal paraffins, when provided with a hydrogenation component, e.g., platinum, hydroisomerization is carried out at a temperature of 100 to 400°C, preferably 150 to 300°C, with a liquid hourly
30 space velocity between 0.01 and 2, preferably between 0.25 and 0.5 employing hydrogen such that the hydrogen to hydrocarbon mole ratio is between 1:1 and 5:1. Additionally, the catalyst

can be used for olefin or aromatic isomerization employing temperatures between 50 and 400°C.

The catalyst can also be used for reducing the pour point of distillate fuels and lubricants. This reduction is carried out at a liquid hourly space velocity between 0.5 and 10, preferably between 0.5 and 5, and a temperature between 200 and 450°C, preferably between 250 and 400°C.

Other reactions which can be accomplished employing the catalyst of this invention with or without a metal, e.g., platinum, or palladium, include hydrogenation-dehydrogenation reactions and desulfurization reactions, olefin polymerization (oligomerization), aromatic alkylation with C₂-C₁₂ olefins or with C₁-C₁₂ alcohols, aromatics, isomerization, disproportionation and transalkylation and other organic compound conversion such as the conversion of alcohol (e.g., methanol) to hydrocarbon.

The invention will now be more particularly described with reference to the following Examples and the accompanying drawing, which is the X-ray diffraction pattern of the ZSM-48 prepared by the method of Example 1.

EXAMPLE 1

To a stirred solution of 1.1g of 45% sodium aluminate (19.5% Na₂O, 25.5% Al₂O₃) in 270 cc of distilled water, 40 g of UltraSil silica (92.4% SiO₂, 0.4% Na₂O) was added. To the resultant stirred mixture, 93 g of ethylenediamine was added. The resultant mixture had a pH of approximately 12.1 and can be described by the following mole ratios of ingredients:

SiO ₂ /Al ₂ O ₃	=	200	Na/SiO ₂	=	200
Diamine/SiO ₂	=	2.5	OH/SiO ₂	=	0.002
H ₂ O/SiO ₂	=	25			

The resultant mixture contained 9 mole % of ethylenediamine in the solvent (ethylenediamine and water).

The mixture was heated for 65 hours at 160°C in an autoclave stirred at 200 rpm, cooled, and filtered. The solid product was then washed with distilled water and dried at 120°C. On analysis, the solid product was identified as ZSM-48 sample having a SiO₂/Al₂O₃ ratio of 190. The ZSM-48 sample contained 0.1 Na ions and 2.3 ethylenediamine molecules per unit cell.

The ZSM-48 sample was found to be pure ZSM-48, as shown by the X-ray diffraction pattern in Figure 1. The ZSM-48 sample is crystalline aggregate having sea urchin-like morphology.

EXAMPLE 2

5 The procedure of Example 1 was repeated except the ratios of reactants were as follows:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	200	Na/SiO_2	=	0.02
Diamine/ SiO_2	=	3.0	OH/SiO_2	=	0.002
$\text{H}_2\text{O}/\text{SiO}_2$	=	18			

10 In this Example, 14 mole % of the solvent was ethylenediamine, and the pH of the starting mixture was 12.4.

The resultant product was again a pure ZSM-48 crystal having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 170. The resultant product contained 0.3 sodium ions and 2.6 ethylenediamine molecules per unit cell.

EXAMPLE 3

15 The starting reaction composition and the procedures of Example 2 were repeated except that the crystallization temperature was 149°C. The resultant product was again a pure ZSM-48 crystal.

EXAMPLE 4

20 This Example shows that an excess of ethylenediamine can promote the formation of zeolites other than ZSM-48. The procedures of Example 1 were repeated except that the amount of water was reduced, raising the molar proportion of ethylenediamine in the solvent to 17 mole %. The initial pH was 12.3.

The crystallization product was mainly ZSM-48, but it contained a small but evident
25 amount of ZSM-5 contaminant.

EXAMPLE 5

This Example shows that a minimum amount of ethylenediamine in the solvent phase is important for rapid and successful ZSM-48 crystallization. The procedure was the same as in Example 1 except that the molar ratios were as follows:

30

$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	200	Na/SiO_2	=	0.02
Diamine/ SiO_2	=	1.5	OH/SiO_2	=	0.002
$\text{H}_2\text{O}/\text{SiO}_2$	=	18			

mole % ethylenediamine in solvent (ethylenediamine and water) = 8

The resultant product was incompletely crystallized ZSM-48. It contained only 20% ZSM-48, together with amorphous material.

EXAMPLE 6

5 The procedure of Example 1 was repeated except the molar ratios were as follows:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	200	Na/SiO_2	=	0.02
Diamine/ SiO_2	=	2.0	OH/SiO_2	=	0.002
$\text{H}_2\text{O}/\text{SiO}_2$	=	30			

mole % ethylenediamine in solvent (ethylenediamine and water) = 6

10 The resultant product is amorphous, after 65 hours at 160°C.

CLAIMS:

1. A method for preparing ZSM-48 which comprises:
 - (a) preparing a reaction mixture comprising a source of silica, a source of trivalent metal oxide, an alkali metal oxide and a directing agent of ethylenediamine in a solvent phase comprising water,
wherein said mixture, in terms of mole ratios of oxides, has the following composition ranges:

$\text{SiO}_2/\text{Me}_2\text{O}_3$:	100 to 1500,
M/SiO_2 :	0 to 0.4,
RN/SiO_2 :	1.0 to 5.0,
OH/SiO_2 :	0 to 0.3, and
$\text{H}_2\text{O}/\text{SiO}_2$:	10 to 100,

wherein Me is trivalent metal, M is alkali metal and RN is ethylenediamine; and
 - (b) maintaining said mixture under crystallization conditions until crystals of said ZSM-48 are formed.
2. The method according to Claim 1, wherein said mixture has the following composition ranges:

$\text{SiO}_2/\text{Me}_2\text{O}_3$:	150 to 500,
M/SiO_2 :	0.001 to 0.10,
RN/SiO_2 :	2.0 to 4.0,
OH/SiO_2 :	0.001 to 0.10, and
$\text{H}_2\text{O}/\text{SiO}_2$:	15 to 40.
3. The method according to Claim 1, wherein the amount of said ethylenediamine is from greater than 5 to less than 20 mole % of the total solvent.
4. The method according to Claim 1, wherein the amount of said ethylenediamine is from 8 to 15 mole % of the total solvent.

5. The method according to Claim 1 wherein the reaction mixture further comprises seed crystals.
6. The method of Claim 5 wherein the seed crystals are in amount of from about 1 to about 5% based on silica.
7. The method according to Claim 1 wherein the crystallization conditions include a temperature of 100 to 200°C for a time of 0.5 hour to two weeks.
8. ZSM-48 prepared by the method of any one of Claims 1 to 7.
9. ZSM-48 of Claim 8 having radial aggregate morphology.
10. A process for converting a feedstock comprising organic compounds to conversion product which comprises contacting said feedstock with a catalyst comprising an active form of the ZSM-48 of Claim 8.

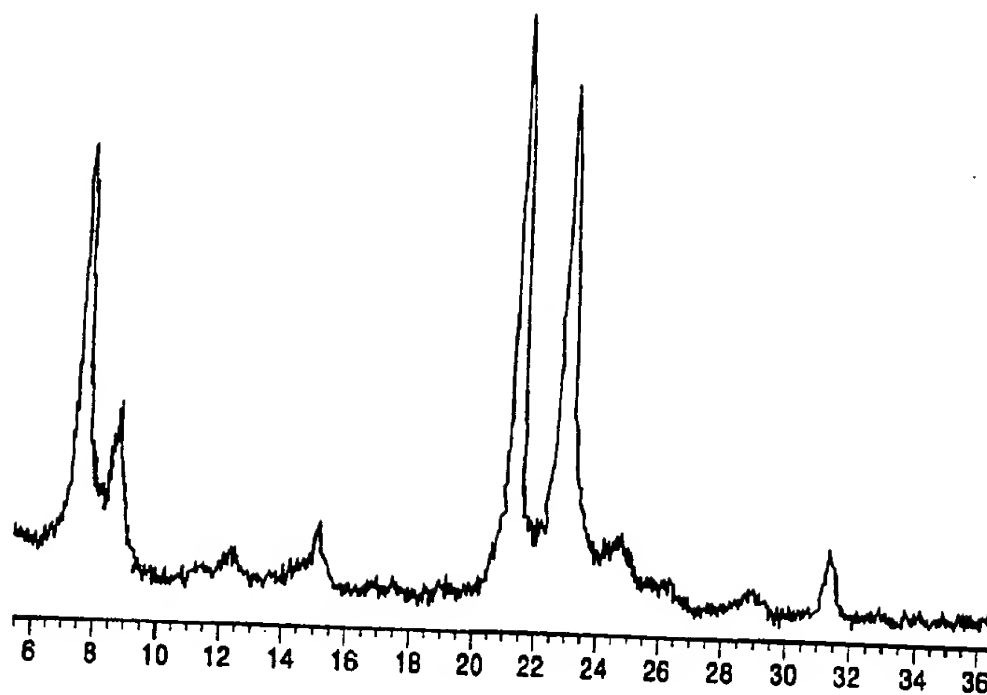


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/00236

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 39/48
US CL : 423/708, 709, 716

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 423/708, 709, 716

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,614,166 A (GEIS et al.) 25 March 1997 (25-03-97).	1-7
A	US 4,581,212 A (ARAYA et al.) 08 April 1986 (08-04-86).	1-7
A	US 4,397,827 A (CHU) 09 August 1983 (09-08-83).	1-10
A	US 4,016,245 A (PLANK et al.) 05 April 1977 (05-04-77).	1-7
A	SZOSTAK, R., HANDBOOK OF MOLECULAR SIEVES, 1992, pp. 551-553.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search
01 FEBRUARY 1999

Date of mailing of the international search report
24 MAR 1999

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